

AFRPL TR-84-036

AD:

Final Report  
for the period  
October 1983 to  
April 1984

## High Temperature Oxidation Resistant Coatings

June 1984

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F04611-83-C-0056

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Rocket Propulsion  
Laboratory**

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				
1. REPORT SECURITY CLASSIFICATION Unclassified		16. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release: Distribution Unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFRPL-TR-84-036		
6a. NAME OF PERFORMING ORGANIZATION Ultramet	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Air Force Rocket Propulsion Laboratory		
6c. ADDRESS (City, State and ZIP Code) 12173 Montague St. Pacoima, CA 91331		7b. ADDRESS (City, State and ZIP Code) AFRPL LKLA - Stop 24 Edwards AFB, CA 93523		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION A.F. Rocket Propulsion Lab.	8b. OFFICE SYMBOL (If applicable) LKLA	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER FO4611-83 C-0056		
8c. ADDRESS (City, State and ZIP Code) Edwards AFB, CA 93523		10. SOURCE OF FUNDING NOS.		
		PROGRAM ELEMENT NO 02301F	PROJECT NO 3258	TASK NO 00
				WORK UNIT NO VM
11. TITLE (Include Security Classification) High Temperature Oxidation Resistant Coatings (U)				
12. PERSONAL AUTHOR(S) Tuffias, Robert H.; Haggerty, John T.; Kaplan, Richard R.				
12a. TYPE OF REPORT Final	12b. TIME COVERED From 83-10 To 84-04	12c. DATE OF REPORT (If Month, Year) 4476		12d. PAGE COUNT 21
13. SUPPLEMENTARY NOTATION				
14. COSATI CODES		15. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB GR		
11	03	Hafnium Oxide Oxidation Resistance		
21	08	Zirconium Oxide Chemical Vapor Deposition		
21. Refractory Metals				
16. ABSTRACT (Continue on reverse if necessary and identify by block number) The feasibility of chemically vapor depositing hafnium oxide and zirconium oxide onto rhenium substrates as potential oxidation resistant materials was investigated. Deposition of the oxide directly is not feasible on materials which oxidize rapidly since direct deposition requires subjecting these materials to an oxidizing environment prior to deposition. Deposition of the oxide was accomplished by first depositing the metal carbide and then oxidizing it. Hard, dense continuous coatings of hafnium carbide which showed good bond strength were achieved. Post coating heat treatment results in a good metallurgical bond between the carbide and the substrate. It has been demonstrated that hafnium carbide/oxide is orders of magnitude more oxidation resistant than rhenium or tungsten.				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS APT <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Kurt Chandler		22b. TELEPHONE NUMBER (Include Area Code) 805 277 5538	22c. OFFICE SYMBOL AFRPL/LKLA	

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## SUMMARY

The feasibility of applying hafnium oxide and zirconium oxide to rhenium substrates as potential oxidation resistant materials was investigated. The results of this investigation demonstrate:

1. The oxides of hafnium and zirconium should be applied to rhenium by first forming the carbide. The oxide is then formed by a substitution reaction with oxygen.
2. Hafnium carbide more easily bonds to rhenium than zirconium carbide.
3. Hafnium carbide can be diffused into the rhenium substrate creating a metallurgical bond between the two materials.
4. Hafnium carbide/oxide coatings increase the oxidation life of rhenium by orders-of-magnitude.

It is recommended that this program be continued with the following emphasis:

1. Determine the deposition parameters required to deposit dense, adherent coatings of zirconium carbide.
2. Deposit and test of hafnium oxide and zirconium oxide within the internal geometry, rather than the external geometry, of test samples.
3. Determine the compatibility of zirconium carbide and hafnium carbide with other refractory materials such as columbium, molybdenum, tungsten, nickel and carbon/carbon.
4. Examine the feasibility of multilayered coatings (i.e. platinum group metals coated with hafnium/zirconium oxide) for added oxidation protection.

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## BACKGROUND

Increased efficiency as well as reduction in mass and size can be achieved for rocket engines and gas turbines by operating at higher temperatures. Examples include the JPL fluorine/hydrazine thruster development program with throat temperatures in the 1500°C to greater than 2000°C temperature range, the space shuttle vernier thruster with maximum temperatures of 1400°C and a desired life of 1,000,000 seconds, the cruise missile turbine, automotive and other gas turbines, etc. In order to retain sufficient strength at temperatures above 1000°C, refractory materials such as molybdenum, tungsten, tantalum, niobium, rhenium or carbon/carbon must be used to fabricate the parts to withstand these temperatures. These materials and their structurally important alloys have notoriously poor resistance to oxidation in the temperature ranges where their strength characteristics are vitally needed. Protection, in the form of coatings, from the oxidizing environment is crucial for achieving the goals of the aforementioned programs.

Currently the only effective materials available for oxidation protective coatings are silicide-based. These materials are not without their limitations. A phenomenon called "pest behavior" has been observed for silicides. At high and low temperatures these materials have good oxidation resistance, however, in intermediate temperature regions they often disintegrate in air. Additionally, due to the difference of coefficient of expansion between the silicide and the base metal, repeated temperature cycling results in cracking of the coating which allows oxygen to diffuse into the cracks and ultimately destroy the base material. The upper limit for silicide coatings is approximately 1400°C but at these temperatures evaporation of the coating is sufficiently high to limit its life due to the limited thickness available from today's technology.

New oxidation resistant coating materials and processes must be developed which will permit operation in the 500°C to 2000°C temperature range. Not only must these materials survive at these temperatures, but they must last for extended periods of time without evaporating, cracking or spalling. Advancement in the technology of rocket engines and gas turbines depends on the development of these new oxidation resistant protective coatings.

High temperature oxidation resistant coatings can be categorized<sup>1</sup> as:

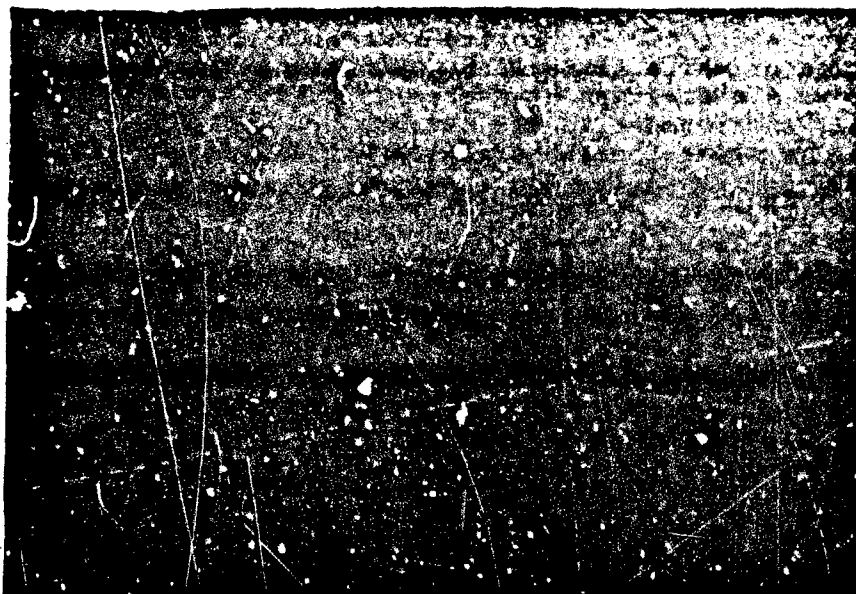
- o Intermetallic compounds that form compact oxide layers (eg  $\text{Al}_2\text{O}_3$  on superalloys,  $\text{HfO}_2$  and  $\text{ZrO}_2$ ).
- o Noble metals and alloys which either don't react with  $\text{O}_2$  (Au) or react slowly forming volatile oxides (Ir and Pt).
- o Intermetallic compounds that form glassy oxide layers (eg silicides, borides).

- o Alloy coatings that form compact oxide layers (Ni and Co based alloys).
- o Stable oxides that provide physical barriers (Cr).

Phase I of this contract was directed toward investigating the first category, specifically zirconium oxide and hafnium oxide on rhenium. Rhenium is of special interest for the new generation of spacecraft thrusters which must operate in an oxidizing environment. Rhenium, the element of atomic number 75, has many properties which make it an attractive candidate for structural operation in the 1500°C to 2500°C temperature range. Rhenium has a melting point of 3180°C, retains substantial strength at high temperatures (14,000 psi ultimate strength and 8000 psi yield strength at 1800°C) and does not oxidize above 2000°C. With proper heat treatment rhenium is ductile at room temperature and is machinable.

In oxygen above 600°C, rhenium undergoes catastrophic oxidation with evolution of white fumes of  $\text{Re}_2\text{O}_7$  (Boiling Point = 363°C). Figure 1 shows a photograph of a rhenium tube that was subjected to a flowing air environment in the neighborhood of 1000°C for several minutes. It is clear from this photograph that in order for rhenium to be a viable material for high temperature operation in an oxidizing environment, an oxidation resistant coating must be provided.

Zirconium oxide and hafnium oxide were chosen for this investigation because these oxides are stable, non-porous oxides which resist further penetration of oxygen<sup>2</sup>. Additionally they have high dissociation temperatures and low vapor pressures over the proposed operating temperature range. Low vapor pressure is an important characteristic with regard to minimizing evaporation of the coating during operation.



**FIG. 1 - OXIDIZED RHENIUM TUBE**

## COATING PROCEDURE

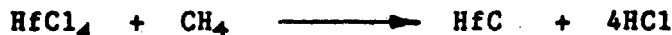
Both hafnium oxide and zirconium oxide coatings can be formed in two ways by chemical vapor deposition: direct deposition of the oxide and deposition of the carbide<sup>3</sup> first and formation of the oxide by a substitution reaction with oxygen. Both methods utilize a similar CVD apparatus (see Figures 2a and 2b) but require different chemicals.

Either hafnium chloride or zirconium chloride can be obtained by heating the metal (sheet clippings) in chlorine gas to about 350 C and feeding the resulting chloride directly into the deposition chamber. Since the reaction which produces the chloride is exothermic, the metal need only be initially heated to start the reaction. Thereafter, the heat generated is sufficient to sustain the reaction.

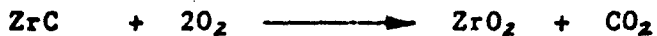
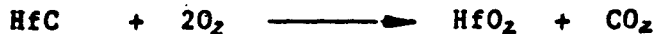
Formation of the oxide directly is obtained by mixing the chloride with water vapor and passing the gas over the substrate which has been heated to 1000°C - 1400°C. The following reactions take place at the substrate surface resulting in deposition of the oxide.



Formation of the carbide is carried out by mixing the chloride with methane and passing the gas over the substrate which has been heated to 1000°C - 1400°C. The following reaction takes place at the substrate surface resulting in deposition of the carbide.



The oxide can then be formed by subjecting the sample to a high temperature oxidizing environment. The rate of oxidation is a function of the oxygen concentration and temperature.



Since both hafnium oxide and zirconium oxide are brittle ceramics, it was felt that high temperature post coating conditioning would be necessary to create a strong mechanical bond. Examination of the binary phase diagrams indicate eutectic melting of Hf-Re at a temperature of 1840°C and Re-Zr at 1600°C. Samples were annealed in argon in the apparatus shown schematically in Figure 3.

Rhenium substrates were made from rhenium tubing with a 0.123 inch OD x .100 inch ID. The substrates were initially 2 1/8 inches long. A molybdenum rod was inserted inside and the ends were welded closed.



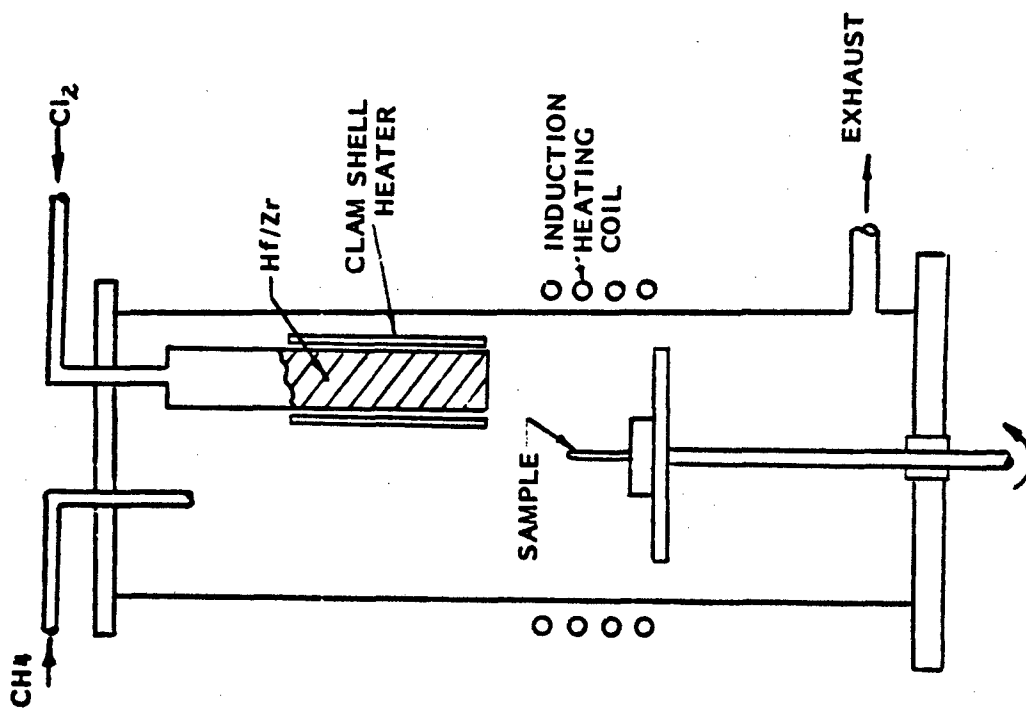


FIG. 2a - CVD SCHEMATIC

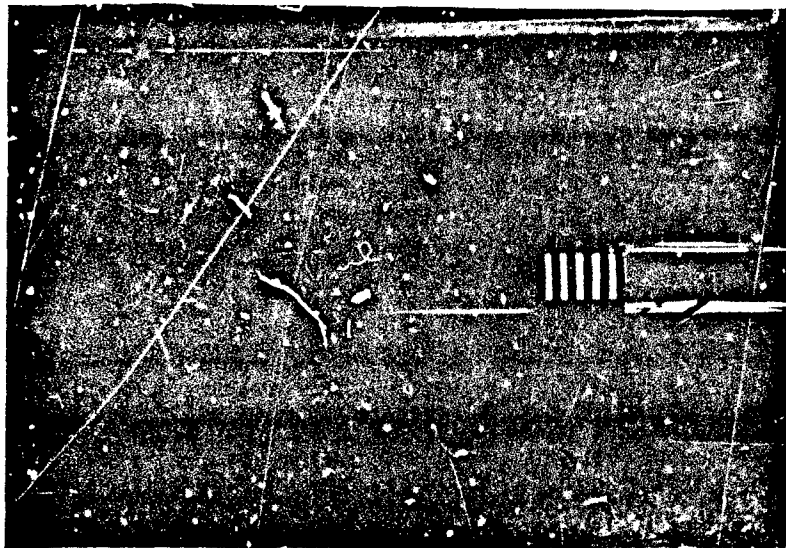


FIG. 2b - CVD APPARATUS

The purpose of the molybdenum rod was to minimize the air inside the sample and to increase the thermal mass. Some rhenium substrates were also made from 1/8 inch diameter rhenium rod. To reduce the cost of the substrates, molybdenum, tungsten and columbium rods were sometimes used. All samples were weighed, measured, and visually inspected under a microscope before and after coating.

The substrates were supported in a graphite holder during coating as shown in Figure 2. By increasing the size of the holder, multiple parts could be coated at the same time. During coating, one end of the part was masked by the holder. In order to completely coat the substrate two runs were required with the ends reversed in each run. This resulted in a problem area which is not inherent in the coating process or the material. Due to this double coating an interface and therefore potential oxygen leakage path exists between the coating layers. Additionally, inconsistent bonds between the two layers may have contributed to thermal cracking upon cooldown. This is not a problem which will be encountered in coating a rocket nozzle since the nozzle need only be coated on the inside and can be supported on the outside. Subsequently test samples were coated only once and the ends kept cool during test.

The carbide coating procedure was as follows:

1. The clam shell heater was heated to 350°C - 400°C prior to heating the substrate/holder.
2. The substrate was heated to 1000°C - 1400°C in argon gas.
3. Chlorine gas was admitted at a nominal flow rate of 800 cc/min.
4. Methane was admitted at a nominal flow rate of 300 cc/min.
5. The clam shell heater was turned off.
6. The coating was allowed to build up to the desired thickness.
7. The methane and chlorine gases were turned off.
8. The induction heater was turned off.
9. The sample was cooled to room temperature in argon.

Initially all coated samples were subjected to a bath of dilute nitric acid to determine if the coating was cracked. The philosophy being that if cracks existed which could not be seen under the microscope, the nitric acid, like oxygen, would attack the substrate. After all samples which were tested in this fashion failed at the ends, it was decided that this test was too severe and was not indicative of the conditions of coating an actual piece of hardware and therefore was discontinued. In the rod shaped test samples, severe thermal stress exist at the ends which have no parallel in an actual device.

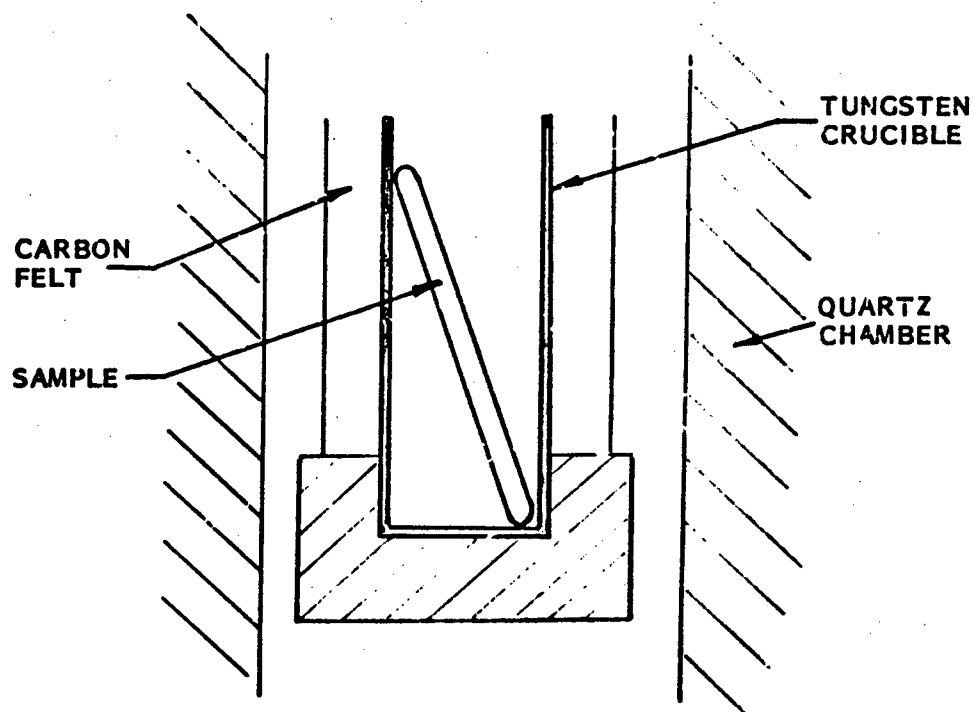


FIG. 3 ANNEALING CHAMBER

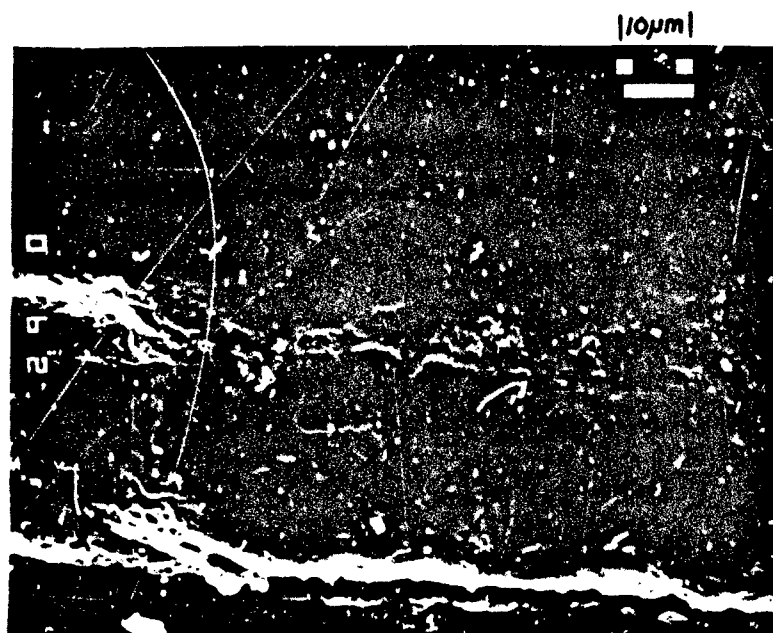


FIG. 4 - HfC COATED RHENIUM AFTER COATING

## COATING RESULTS

### Zirconium and Hafnium Oxides

Attempts at direct deposition of the oxides of hafnium and zirconium were unsuccessful. Experiments were run at various substrate temperatures, gas mixture ratios and gas pressures. Introduction of the water vapor resulted in a surface reaction at the substrate which inhibited deposition of the metal oxides. Any deposit which was obtained was not continuous and easily peeled off.

### Zirconium Carbide

Continuous films of zirconium carbide about 0.0015 - .002 inch thick were obtained at a substrate temperature of about 1400°C. Efficiencies were typically very low, about 12 - 14%. In most cases the coatings spalled off or were easily scraped off. In one case, the coating looked extremely good but upon subjecting it to a bath of dilute nitric acid (to check for cracks), large sections flaked off.

### Hafnium Carbide

Experiments were conducted at various substrate temperatures, gas ratios and flows, and using different substrates including rhenium, tungsten, columbium and molybdenum.

Hard, dense, adherent coatings on rhenium were obtained at a substrate temperature of 1350°C. Coating thicknesses of .001 to .004 inch were controllable and reproducible with efficiencies of 30 - 40%. Deposition rates were approximately .010 - .012 inch per hour. Similar results were achieved with tungsten, columbium and molybdenum substrates.

Figure 4 shows a 1000X photograph of a cross-section of a hafnium carbide coating on a rhenium tube prior to annealing. The coating thickness is approximately .0015 inch. Although no diffusion layer can be observed the materials are in intimate contact.

In an attempt to obtain a metallurgical bond between the hafnium carbide and the rhenium, samples were annealed at 1700°C and 2000°C for 30 minutes each. Figure 5 shows a photomicrograph at 4500X of the sample annealed at 1700°C. A diffusion layer in the rhenium 20 - 30 microinches thick is indicated by the darker band adjacent to the hafnium carbide. Figure 6 shows a photomicrograph at 4500X of the sample annealed at 2000°C. The diffusion layer shown here is greater than 0.0001 inch thick.

The original method of oxidation testing required that the sample be completely coated. In order to coat both ends the sample was coated twice, resulting in a double layer on most of the sample. A photomicrograph (see Figure 7) of an area which had a double coating revealed that no bond existed between the two layers. High temperature post-coating annealing or sputter cleaning prior to depositing the second layer may result in a bond between the two layers.

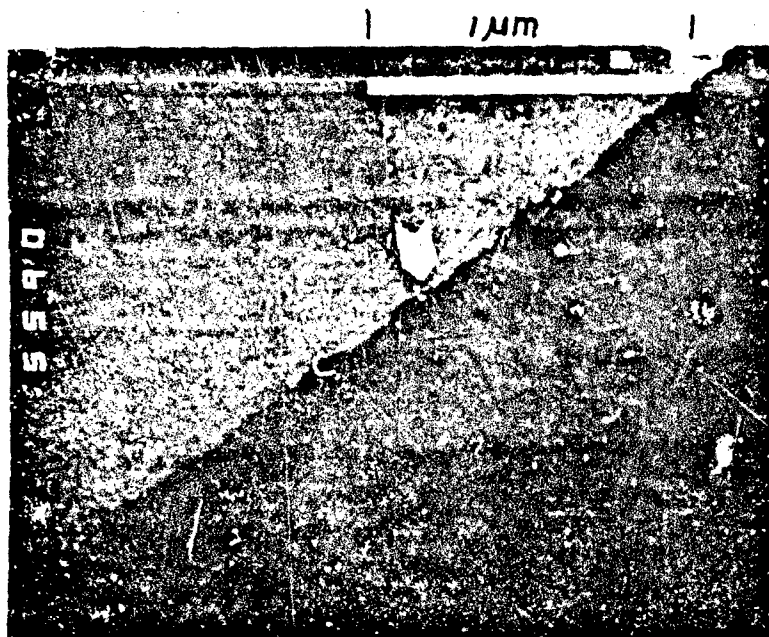


FIG. 5 - HfC ON RHENIUM AFTER  
ANNEALING AT 1700°C FOR 30 MINUTES

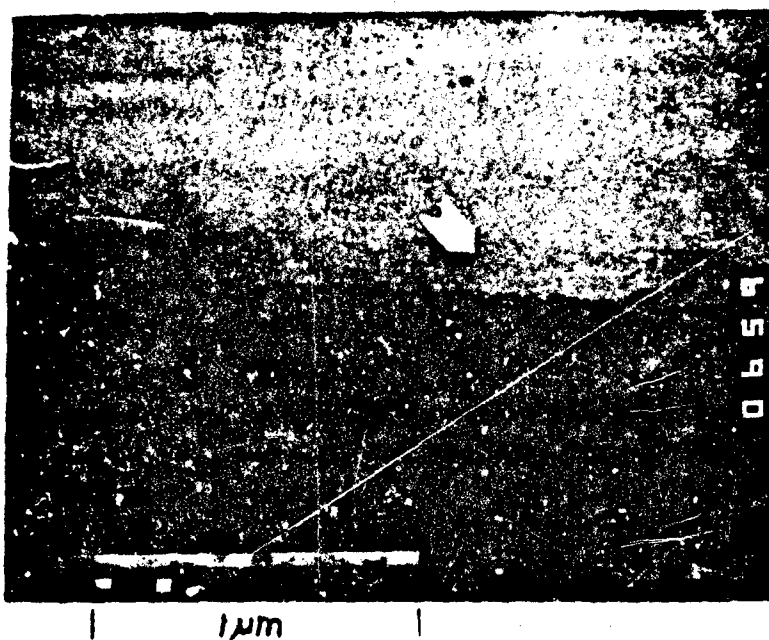


FIG. 6 - HfC ON RHENIUM AFTER  
ANNEALING AT 2000°C FOR 30 MINUTES

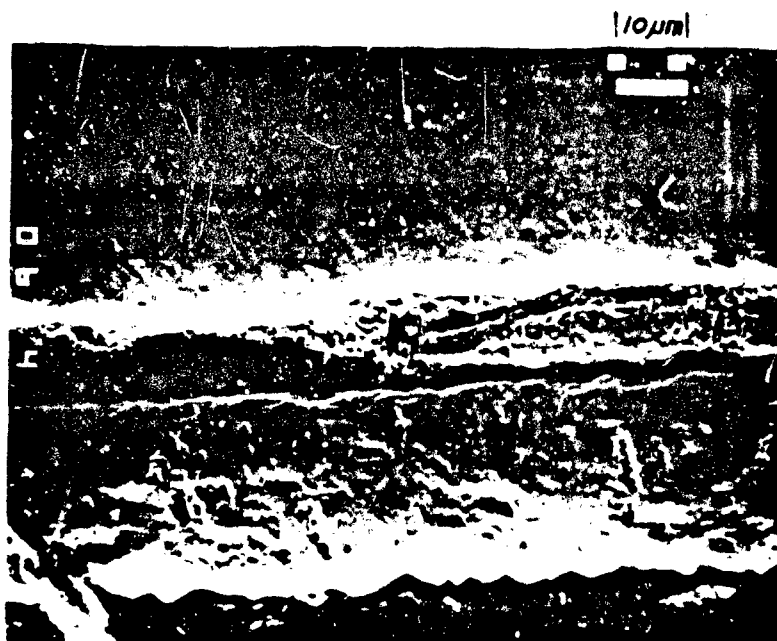


FIG. 7 - DOUBLE LAYER OF HfC ON RHENIUM

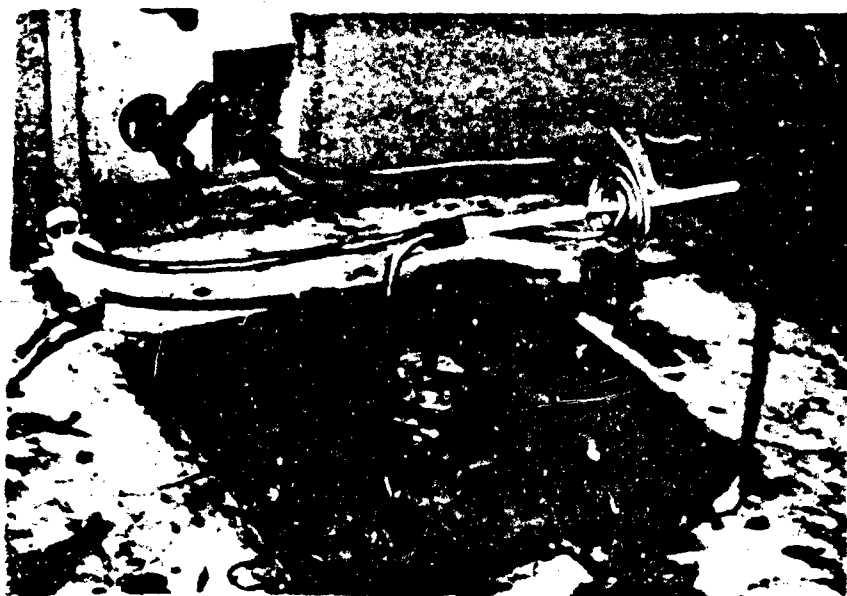


FIG. 8 - OXIDATION TEST APPARATUS

## OXIDATION TEST RESULTS

Oxidation tests were performed by induction heating the sample in air to the desired temperature using the apparatus shown in Figure 8. Due to the difficulty in coating the ends of the sample and to eliminate problems associated with double-layered coatings, the apparatus was designed to heat only the central region of the sample. The ends were kept cool in flowing argon.

Figure 9 shows the results of an oxidation test on a rhenium tube with .010 inch wall thickness at 1000°C - 1500°C for less than 2 minutes. Dense white fumes of  $\text{Re}_2\text{O}_7$  are evolved in air at temperatures above 600°C. Since the tube was eaten away so quickly, it was not possible to maintain constant temperature.

Figure 10 shows a photomicrograph and the results of an oxidation test on a bare tungsten rod after 9 minutes of exposure at 1050°C. The oxide layer developed during this period was 0.0025 inch thick, with 20-30% due to swelling.

Figure 11 shows a photomicrograph of the results of an oxidation test on a tungsten rod coated with 0.0025 inch thick hafnium carbide. The sample was exposed to air for 10 minutes at 1100°C. Note that approximately one half of the thickness of the hafnium carbide has oxidized, but the tungsten substrate has been untouched. Oxidation of hafnium carbide results in a color change from dark gray to white but no growth of the outside diameter.

Tests of continuous (no temperature cycling) oxidation in air of hafnium carbide on tungsten substrates at various temperatures from 1000°C to 1500°C resulted in an increasing rate of oxidation as a function of temperature. No quantitative data was obtained but in all cases no growth of the outside diameter was exhibited. No samples were oxidized for times long enough for the carbide coating to be completely oxidized. It may well be that when the oxide layer gets thick enough, it becomes completely impervious to oxygen.

Tests of oxidation resistance of hafnium carbide approximately 0.001 inch thick on rhenium for 10 continuous minutes at 1600°C indicated no damage to the rhenium substrate. Although no surface cracks were visible upon room temperature examination, smoke appeared approximately 2 minutes into the second cycle. Room temperature examination revealed surface cracking. More complete diffusion of the coating into the substrate should reduce the stresses which cause the cracks.

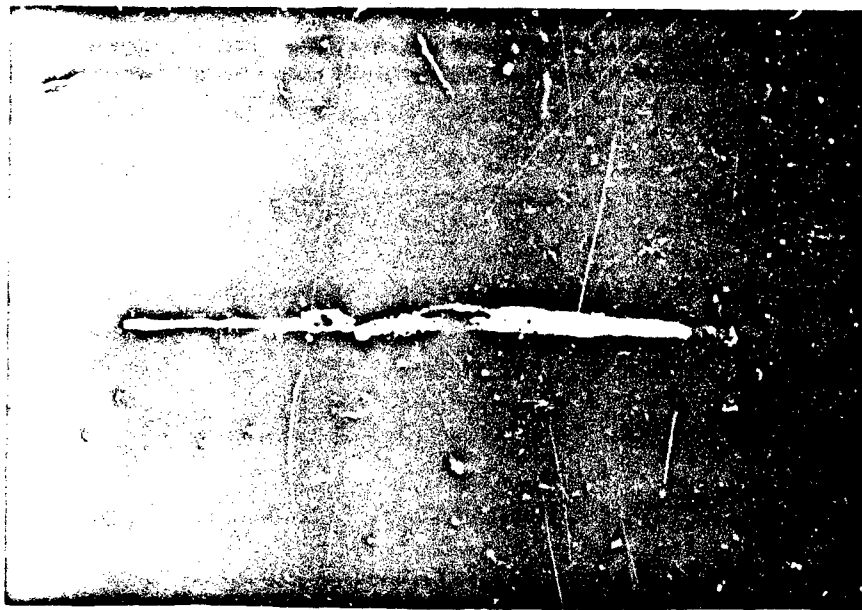
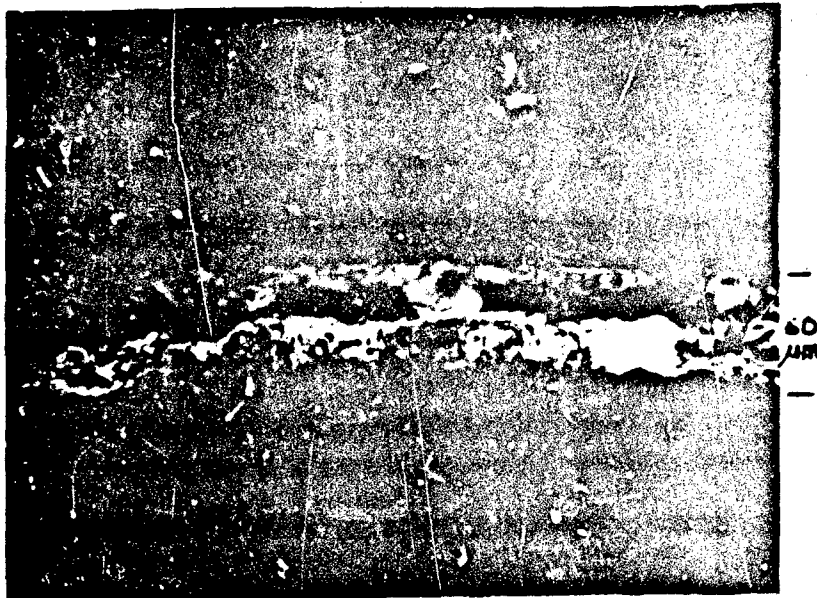


FIG. 9 - OXIDATION OF UNCOATED RHENIUM TUBE



FIG. 10 - OXIDATION OF PURE TUNGSTEN ROD





**FIG. 11 - OXIDATION TEST OF HfC COATED TUNGSTEN ROD**

## DISCUSSION

Ultramet investigated the feasibility of applying zirconium oxide and hafnium oxide by CVD to refractory metal substrates for use as oxidation resistant coatings. The program consisted of two separate areas: coating applications and oxidation testing.

### 1. Coating Application

Based on the experiments performed, direct deposition of hafnium or zirconium oxide, which requires subjecting the heated specimen to water vapor, is detrimental to the specimen. Since rhenium reacts so violently with oxygen and the object of this program is to develop coatings which protect rhenium from oxygen, it is not surprising that subjecting the sample to water vapor would result in a surface reaction which would inhibit the deposition of the metal oxides. Clearly successful deposition of the oxide requires deposition of the carbide first.

The deposition of zirconium carbide on rhenium did not result in adherent coatings but it is felt that further effort is warranted in this area. In most cases, the application of oxidation resistant coatings is required on the inside of hollow structures rather than the outside. Since the stress distribution on internal coatings is compressive in nature and the strength of ceramics is greater in compression than tension, internal coatings of zirconium carbide would likely be more successful. Additionally and probably more important, it has been found that surface treatment and outgassing are extremely important when depositing coatings onto rhenium. This area should be investigated. It is felt that further effort on the deposition of zirconium carbide will provide successful results.

The greatest success was with hafnium carbide. Hafnium carbide was deposited onto rhenium and tungsten with good bond strength, density, continuity and thickness. Deposition rates of the order .010 inch per hour were achieved with high efficiencies. Additionally, it was found that high temperature heat treatment results in the hafnium carbide diffusing into the rhenium substrate achieving a good metallurgical bond. Further investigation in this area with additional substrate materials is recommended.

## 2. Oxidation Testing

Hafnium carbide is orders-of-magnitude more oxidation resistant than rhenium, tungsten, molybdenum or columbium. When subjecting hafnium carbide to a continuous, high temperature oxidizing environment, the oxide formation begins at the surface and progresses inward, the speed of which is a function of temperature. During this process, the surface remains intact without swelling. It is not currently known whether the oxide becomes impermeable to oxygen prior to complete oxidation of the carbide. Another question is whether in an actual application it is better to let the oxide form during operation or to preoxidize the carbide. It is conceivable that a low temperature, long time oxidation of the carbide will form a more dense and impermeable oxide. These questions should be investigated further.

Temperature cycling of hafnium carbide coatings resulted in cracking the coating, allowing a path for the oxygen to reach the substrate. One reason for this occurrence is due to the fact that the outside coating is put into tension during cool down because HfC has a lower thermal expansion than metals. Internal coatings should be more crack resistant. Additionally, long time, high temperature annealing of the coating should result in a larger diffusion boundary which will permit the stresses to be distributed into the metal substrate. Currently, it is not clear whether thin or thick coatings are better. These areas should be investigated.

Hafnium carbide is also a potential material for use in multilayered oxidation resistant coatings. For example, a layer of hafnium carbide on top of an iridium layer will decrease the evaporation of the iridium. Even if the hafnium oxide cracks, the evaporation will be minimized and orders-of-magnitude less oxygen will be permitted to attack the iridium.

## RECOMMENDATIONS

Hafnium carbide coatings have been demonstrated to increase the oxidation resistance of rhenium and tungsten by several orders-of-magnitude. It is likely that zirconium carbide coating techniques can be developed which will also prove promising. In order for a viable oxidation resistant hafnium and zirconium coating technology to be available to industry a Phase II program is recommended. This Phase II program should include the following:

1. Determine the oxidation resistance characteristics of hafnium oxide and zirconium oxide. This is useful as baseline data to verify the available data and extend the range to 2000°C. Oxidation resistance will be measured by determining the weight and dimensional changes of solid samples. The oxidation resistance test facility fabricated in Phase I can be used for this purpose. In order to determine which material is best for a specific mission, this information is necessary.
2. Design, fabricate and test a facility for measuring oxidation resistance on the inside of tubular samples. Since oxidation resistant coatings for thrust chambers will be on the inside of the device, a geometry should be tested which more closely simulates actual operation.
3. Determine the deposition parameters required to deposit dense adherent coatings of zirconium carbide. Phase I demonstrated that dense coatings of zirconium oxide can be achieved but adherence to rhenium was not achieved. Because of its importance as an oxidation resistant material, the zirconium oxide effort should be extended. Other substrates should be tried and adhesion to concave rhenium substrates assessed.
4. Extend the techniques learned in Phase I to depositing hafnium carbide and zirconium carbide onto additional substrates: molybdenum, columbium, nickel, and carbon/carbon. This should include direct deposition and using rhenium as an intermediate layer.
5. Assess the prospect of depositing a ceramic layer ( $ZrO_2$  or  $HfO_2$ ) on top of a platinum group metal coating as a method of inhibiting evaporation of the platinum group metal.
6. Modify the techniques developed in Phase I for plating outside surfaces to permit depositing hafnium carbide and zirconium carbide on the inside of tubular structures. Geometric effects of deposition require developing a different deposition mechanization for depositing on the inside of tubular structures than on the outside.

7. Do metallography of selected coated specimens to determine composition, grain morphology, defect structures and boundary conditions.
8. Measure the mechanical properties of the coated parts to determine whether any adverse effects on strength, ductility, etc. have occurred as a result of the oxidation resistance process.
9. Test the oxidation resistance of the various substrate/coating combinations. This would involve measuring the effects of temperature, thermal shock and temperature cycling.
10. Provide oxidation resistant coatings to rocket engine manufacturers for test under actual conditions. Ultramet is in continual communication with the rocket development people at Aerojet, Rocketdyne, Marquardt, Rocket Research and JPL. All have expressed interest in this program and their willingness to provide hardware for coating and test.

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